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# Thermodynamic properties in some aqueous biological fluid mixture

O P Chimankar*[b], K G Rewatkar[a] and V A Tabhane[a]

[a]Department of Physics, Institute of Science, Nagpur-440 001, Maharashtra, India

[b]Department of Physics, M B Patel College, Sakoli-441 802, Bhandara, Maharashtra, India

E-mail : OP_Chimankar@yahoo com

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**Abstract** . The ultrasonic velocity and their related thermoacoustical parameters were successfully employed to understand the structural changes and the nature of molecular interactions in the mixtures Ultrasonic velocity, density and viscosity in aqueous solution of glycine, L-arginine and L-histidine and the thermodynamic parameters *viz* adiabatic compressibility, thermal expansion coefficient, specific heat, internal pressure, van der Waals' constant have been computed from the experimental data These measurements were carried out by using the ultrasonic pulse echo overlap (PEO) technique at a frequency of 2 MHz at temperature 298 K. The observed and calculated thermodynamic parameters show nonlinear behaviour with increase in molar concentration of amino acid This indicates the presence of molecular interaction, complex formation, solute-solvent, dipole-dipole and hydrogen bonding interaction in the biological fluid mixtures

**Keywords** : Ultrasonic velocity, thermoacoustical parameters, biological fluid mixture

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The study of propagation of ultrasonic wave in liquid and liquid mixtures is well established for examining the nature of intermolecular and intramolecular interaction in liquid system [1] Recently, there has been an increased interest in the state of water in the living cell. For the knowledge of water-protein interaction, it is necessary to understand the role and interaction of biological macromolecules in living organism [2]. In recent years, considerable interest has been developed in understanding the nature of interaction between amino acids and water by studying its partial molar volume [3], heat capacities [4,5] and compressibility [6]. Nambinarayanan [7] have explained that the nature of molecular interaction in aqueous biological solution is rather complex. The present note reports the ultrasonic and related thermodynamical parameters in the aqueous solution of biological material *viz* glycine, L-histidine and L-arginine.

According to the molecular weight, the solution of glycine, L-histidine and L-arginine are prepared by dissolving into 100 ml triple distilled water. These aqueous biological solutions having molarity 0.01 M are mixed with water in different concentrations. Total 50 ml solution was prepared for the measurement of ultrasonic velocity at a frequency of 2 MHz and was measured by using an automatic ultrasonic attenuation recorder (AUAR-102) (Innovative Instrument, Hyderabad) and a frequency counter APLAB-1116. The density and viscosity were determined by using hydrostatic sinker method and Ostwald's viscometer respectively A specially designed and fabricated stainless steel cell was used for the measurement of ultrasonic velocity The temperature of fluid mixtures was maintained constant at 298 K by the use of thermostat U-10.

In aqueous glycine, the variation of ultrasonic velocity ($u$) with molar concentration ($C_m$) is found to exhibit a peak at $C_m$ of 0.0003 (Figure 1a) while the adiabatic compressibility ($\beta_a$), volume expansivity ($\alpha$) variation with $C_m$ shows a dip at corresponding concentration (Figures 1a, 2a) The variations of internal pressure ($P_i$) and specific heat ($C_p$) with $C_m$ are both found to exhibit a peak at $C_m$ of 0 001 and a dip at 0.0003 (Figures 3a, 4a). The van der Waals' constant ($b$)

* Corresponding Author

initially decreases with $C_m$ and exhibits a dip at 0.0005 (Figure 5a).

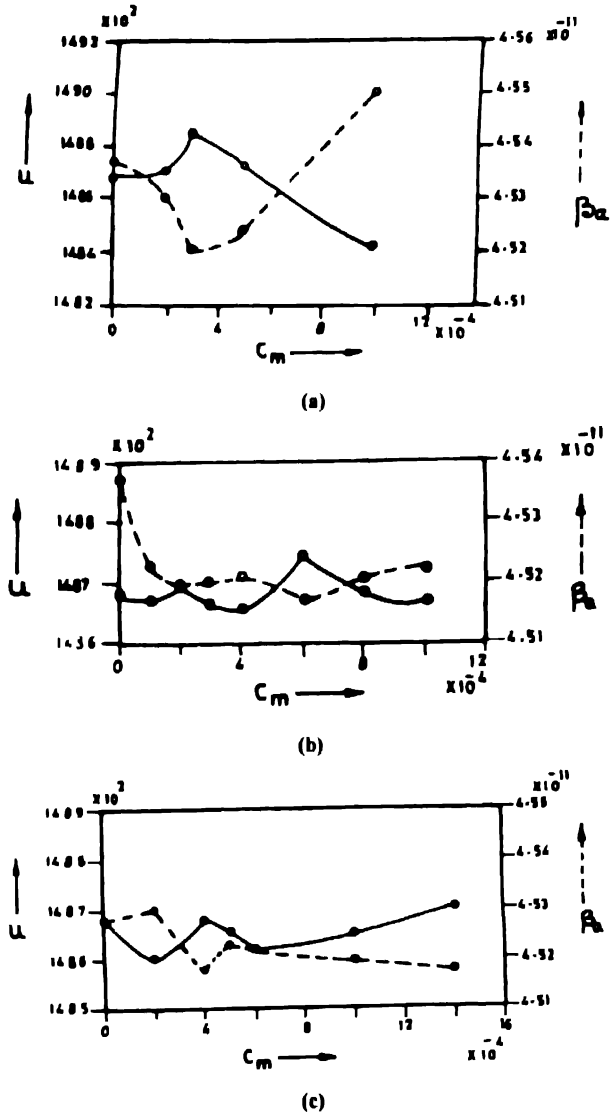


**Figure 1.** Variation of ultrasonic velocity ($u$) and adiabatic compressibility ($\beta_a$) with molar concentration ($C_m$) in aqueous (a) glycine, (b) L-histidine and (c) L-arginine

In aqueous histidine, the variation of ultrasonic velocity (Figure 1b) shows two small peaks at $C_m$ of 0.0002 and 0.0006 while the adiabatic compressibility (Figure 1b) shows small dips at corresponding concentrations. The volume expansivity with $C_m$ shows a dip at 0.0006 (Figure 2b). The variations of internal pressure (Figure 3b) and specific heat (Figure 4b) with $C_m$ exhibit two peaks at molar concentrations of 0.0002 and 0.0004. The trend of van der Waal's constant ($b$) with $C_m$ is found to show non-linear behaviour with small maxima and minima (Figure 5b).

In aqueous arginine, the curve of ultrasonic velocity (Figure 1c) with $C_m$ shows a peak at 0.0004 while the adiabatic compressibility (Figure 1c) shows a dip at the corresponding concentration. The variations of volume

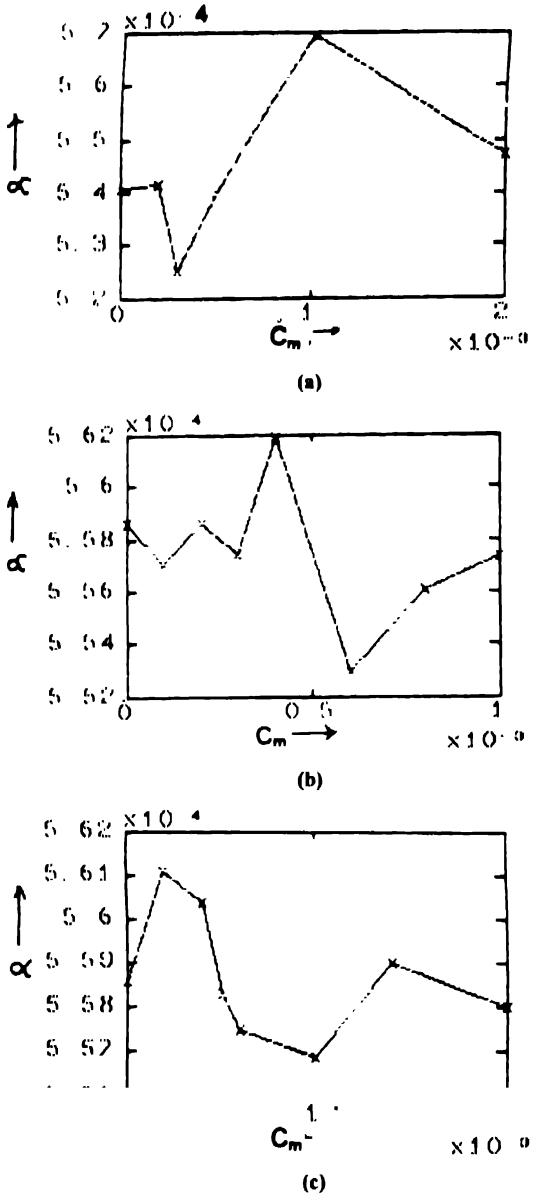


**Figure 2.** Variation of volume expansivity ($\alpha$) with molar concentration ($C_m$) in aqueous (a) glycine, (b) L-histidine and (c) L-arginine

expansivity, internal pressure and specific heat with $C_m$ are all found to exhibit a peak at 0.0002 and a dip at 0.001 (Figure 2c, 3c, 4c). The variation of $b$ with $C_m$ exhibits a dip at 0.0002 and a peak at 0.0004 (Figure 5c).

When amino acid dissolves in water, amines and carboxylic groups strongly interact and are present in ionic forms ($NH_3^+$ and $COO^-$). A more dense packing of water molecules in the vicinity of such ions suggest that cohesion through hydration is more probable [8]. Specific heat values are considered to be sensitive to the arrangement of the

solvent and solute molecules [9]. It is the indication of solute-solvent interaction. The internal pressure in solution could be used for studying the molecular association through hydrogen bonding [10].

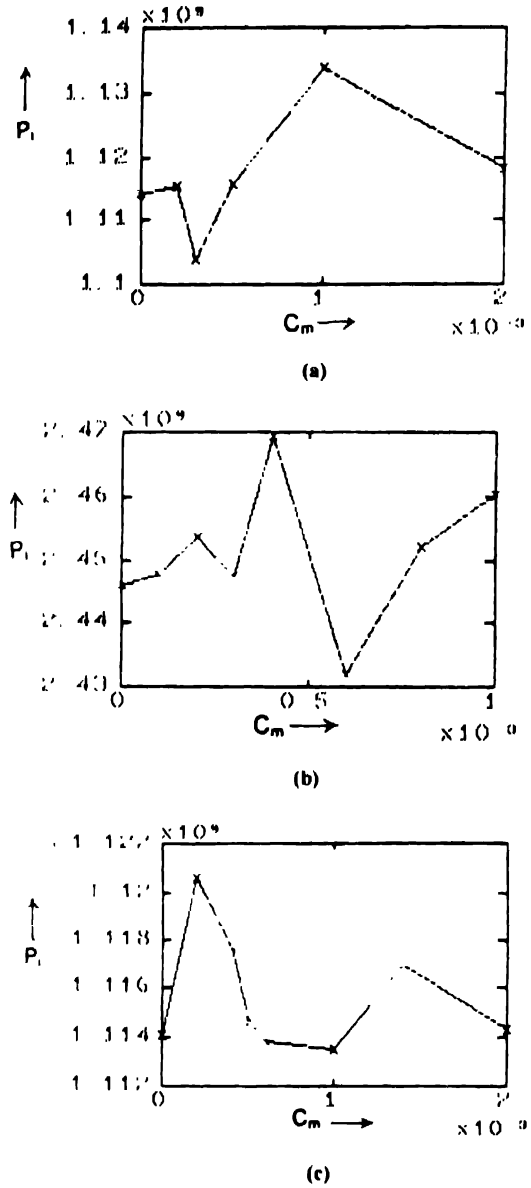


Figure 3. Variation of internal pressure ($P_i$) with molar concentration ($C_m$) in aqueous (a) glycine, (b) L-histidine and (c) L-arginine

The variation of the thermodynamical parameters with increase in molar concentration is found to show non-linear behaviour. This non-linearity confirms the presence of complex formation, solute-solvent interaction [11] and weak association due to hydration [12]. The small increase in ultrasonic velocity may be attributed to the breaking of clusters by the amino acid molecules resulting in enhancing the close-packed structure of water. This increases cohesion between water molecules, hence the adiabatic compressibility decreases with increase in molar concentration. This indicates the enhancement of degree of association [13] due to the larger probability of formation of hydrogen bonding in between biomolecules and water molecules. Thus the

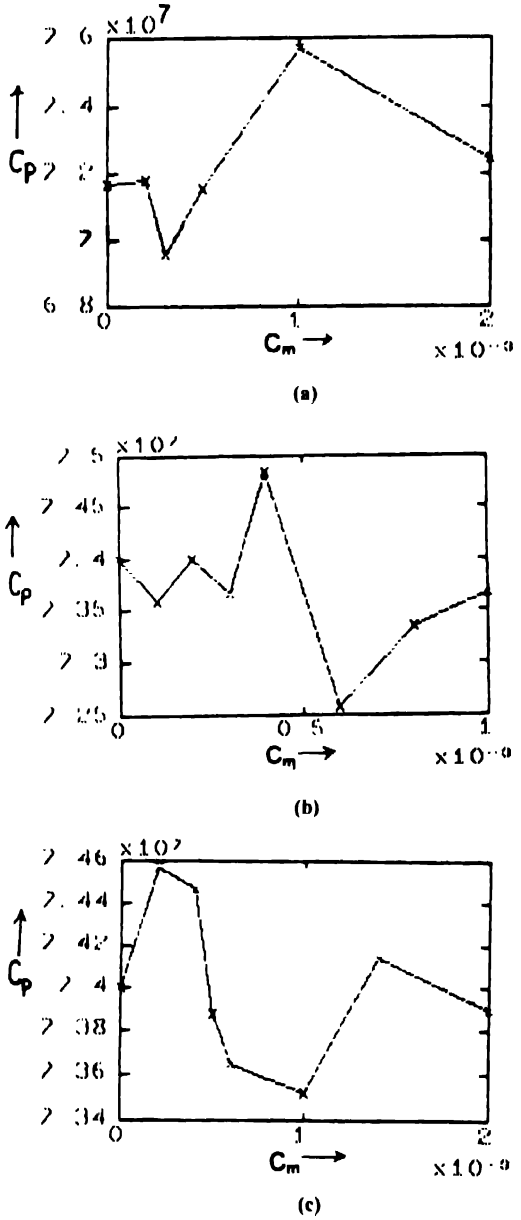


Figure 4. Variation of specific heat ($C_p$) with molar concentration ($C_m$) in aqueous (a) glycine, (b) L-histidine and (c) L-arginine.

intermolecular distance decreases with increase in molar concentration showing that the cohesive or intermolecular forces are stronger.

The specific heat values in biological fluid mixtures are found to decrease or increase with molar concentration as compared to water. The decrease in specific heat shows structure-breaking tendency due to electrostriction of $COO^-$ and $NH_3^+$ groups. These are separated by only one $-CH_2$

group; as a result, the hydration spheres of the two overlaps are observed. The orientation of water dipoles around $COO^-$ and $NH_3^+$ is exactly opposite due to the reverse polarity. Hence in the overlap region, water molecules exist in a

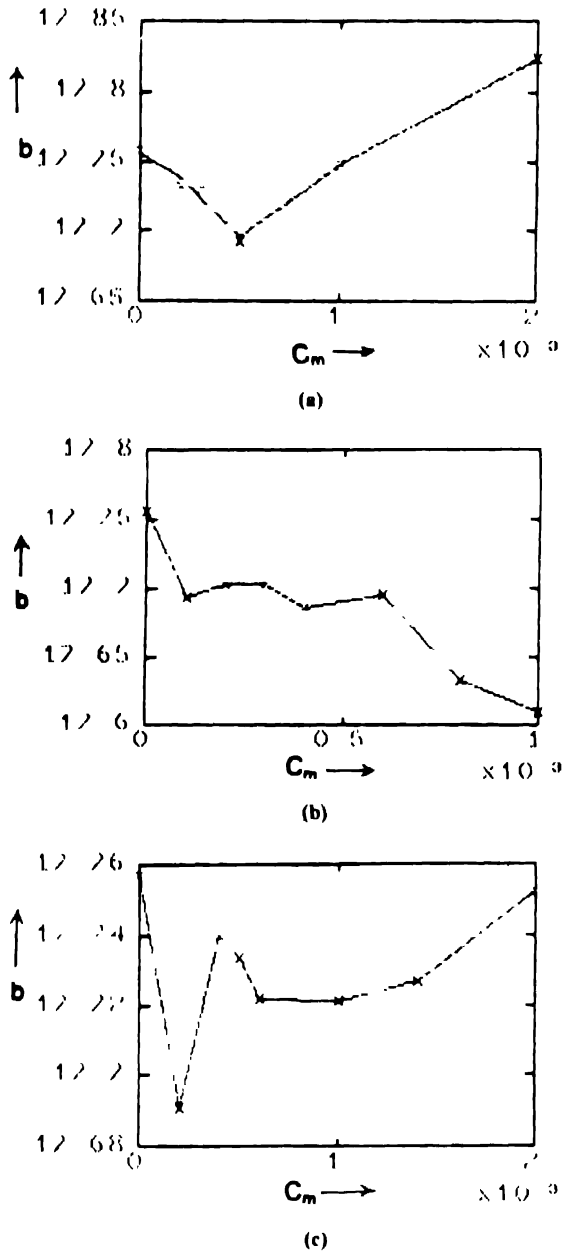


**Figure 5.** Variations of van der Waals' constant ($b$) with molar concentration ($C_m$) in aqueous (a) glycine, (b) L-histidine and (c) L-arginine

relatively disordered state. The increased specific heat shows structure-making ability *i.e* hydrophobic hydration or structure-enhancing propensity of amino acids with rise in molar concentration of amino acid. During this time, electrostriction effect (structure breaking) due to dipolar character remains constant and independent of side chain or groups.

The internal pressure is found to increase or decrease in aqueous amino acids. The internal pressure increases with molar concentration indicates the orientation of the solvent molecules around the ions. This may be due to the influence of electrostatic field of ions *i.e.* the solution becomes harder to compress. This also shows the associating tendency of the molecules whereas the reduction in internal pressure shows the dissociating tendency of the molecules in bio-solutions. The increase in the value of van der Waals' constant $b$ with molar concentration can be caused due to dissociation of a closed packing of the molecules inside the shell.

From the above studies, the major conclusions may be summarised as :

(i) The non-linear variation of thermodynamical parameters with molar concentrations of amino acids provides useful information about the nature of intermolecular forces existing in the mixture.

(ii) The non-linearity confirms the presence of complex formation, molecular association or dissociation in biological fluid mixture may be due to the breaking or making of hydrogen bonding in water and amino acid molecules.

(iii) The observed complex formation and molecular association in present liquid mixtures may be due to the formation of hydrogen bonding in the molecules of water and amino acid. This show the tendency of solute-solvent interaction and weak association arising due to hydration.

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